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(54) Title: IMPROVEMENTS IN THE CONVERSION OF CHEMICAL MOIETIES

(57) Abstract

A process for the conversion of a chemical moiety, which may be gaseous, liquid or a solid in fluidised form, in which the chemical moiety is reacted with a plasma or with a reagent generated by the interaction of plasma with another component, which may be a solid.

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agent generated by the interaction of plasma with another component, which

IMPROVEMENTS IN THE CONVERSION OF CHEMICAL MOIETIES

This invention relates to improvements in or relating to processes for converting fluidised chemical moieties.

In general, reactions need energy to initiate the reaction. Where this activation energy is high, the reaction is commonly carried out at high temperature and/or pressure. We have now found a new method of supplying the energy which enables reactions to be carried out at lower pressures, e.g. atmospheric pressure or sub-atmospheric pressure and/or lower temperatures. The reactions therefore require less energy and are safer. The ability to carry out the reactions at lower temperatures and pressures also means that cheaper materials and simpler methods of construction can be used in the construction of the reaction vessels.

Alternatively improved results may be obtained at the higher temperature and/or pressure.

In accordance with the present invention, there is provided an improvement in processes for the conversion of a chemical moiety characterised in that the chemical moiety is in a fluid phase and said moiety is reacted with a plasma or with a reagent generated by the interaction of the plasma with another component. The process may involve the use of a catalyst.

It is to be understood that the term conversion, as used herein, relates to the conversion of a material to a desired product and not merely to surface modification. It is also to be understood that the invention relates to conversion of one chemical by treatment with a plasma which is not derived from the same molecule, and thus does not relate, for example, to plasma polymerisation.

IE CONVERSION OF CHEMICAL MOIETIES

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The moiety may be an element or a compound and may be gaseous or liquid or it may be a solid which is in fluidised form. Where the chemical moiety is a liquid, e.g. through which the plasma is bubbled, it may be provided as such or as an aerosol, in which case the carrier gas may be or comprises the gas that is excited to plasma.

In the embodiment where the moiety is reacted with a reagent generated by the action of the plasma on another component, the plasma may be directed, for example, onto the surface of a solid to produce reactive species which react with the moiety. The solid may be a catalyst, for example. Alternatively, the reactive species may be generated from the action of the plasma on a liquid.

Plasma is normally generated from a gas; however, a liquid may also be used. For example, water may be excited to form plasmas of hydrogen and oxygen.

Any suitable means may be employed for generating the plasma. For example, it may be generated by DC glow discharge, AC electric field, plasma torch and heat, all of which may be pulsed. The heat may be generated by laser.

Alternating currents for generating the AC plasmas are preferably those having a frequency of $1\text{-}10^{12}$Hz, more preferably $10^{3}\text{-}10^{9}$Hz. It will be understood, however, that in some countries the frequencies that may be used are limited, e.g. because of the risk of interference with radio transmissions. For example, in Great Britain, a frequency of 13.56MHz is set aside by the Government for such experiments and will not therefore interfere with radio transmissions. Other frequencies can be used, provided that the Government is advised of the intention to use these frequencies.

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Frequencies of less than 1 Hz may also be used. However, such frequencies may give rise to alternating or periodic glow discharge rather than a continuous plasma. Such discharges are advantageous when the power input has to be minimised or to provide additional control of the reaction.

Plasma that is generated by alternating current at radio-frequency is normally generated from gases at sub-atmospheric pressure. Pressures of from 100 to 10^{-3} torr are suitable. However, the pressure used is dependent on the power loadings. Therefore, if a sufficiently high power loading is available, it is possible to excite gas to plasma at a pressure above 100 Torr, if desired.

However, plasmas generated by other means such as arc plasma or plasma torch are often generated at a variety of pressures ranging from sub- to super- atmospheric.

Where the reaction vessel is large, as in an industrial scale reaction, it is preferable to generate the plasma at lower frequencies such as 40kHz so as to reduce the likelihood of the plasma varying in intensity across the vessel. If higher frequencies are used, nodes and antinodes of plasma intensity may be created which may result in power loss and a reduction in the efficiency of the process.

A mixture of more than one plasma may be employed and where more than one gas or liquid is excited to plasma, this may be effected before or after mixing.

While the process of the invention may be applied to conversions generally, and more particularly gaseous reactions, it is particularly useful for converting toxic gases, such as are present in internal combustion engine exhaust gases and gaseous industrial emissions, to non-toxic waste products. Either or both of the toxic gas and

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the gas employed to convert it to a non-toxic product may be converted to plasma.

Internal combustion engine exhaust gases and other exhausts from hydrocarbon burning consist mainly of CO, NOx and gaseous hydrocarbons. The NOx can be detoxified by reaction with CO or unburned hydrocarbons to give N_2 and CO_2. Excess carbon monoxide and unburned hydrocarbon fuel are normally oxidised to CO_2 and water.

Examples of the detoxification of industrial gaseous emissions include the denaturing of NOx to water and nitrogen gas using hydrogen plasma, the dehalogenation of organic molecules using hydrogen plasma and the removal of odour from industrial emissions such as the emissions from fat rendering, glue and size manufacturing, tanning, fish meal processing, polyvinyl chloride and polyurethane manufacturing and cutting, food manufacturing, coffee roasting, manure processing and meat processing industries. Some of these detoxification reactions may require the presence of a catalyst.

Exhaust gases and gaseous industrial emissions commonly include fine particulate matter dispersed in the gas. The process of the present invention may be used to convert the particular moieties to more acceptable gaseous products, to soluble products which can then be removed from the gas e.g. by washing, or to liquids which can be separated from the gas. For example, carbonaceous material such as soot can be treated with an oxygen plasma to form carbon dioxide.

Some reactions have such a high energy of activation that they have to be carried out at very high temperature and/or be initiated by free radicals even in the presence of a catalyst. We have now found that if such reactions are carried out in the presence of plasma in accordance with

convert it to a non-toxic product may ma.

ɜngine exhaust gases and other exhausts rning consist mainly of CO, NOx and s. The NOx can be detoxified by unburned hydrocarbons to give N_2 and ıonoxide and unburned hydrocarbon fuel d to CO_2 and water.

ɜtoxification of industrial gaseous he denaturing of NOx to water and ydrogen plasma, the dehalogenation of ing hydrogen plasma and the removal of l emissions such as the emissions from and size manufacturing, tanning, fish olyvinyl chloride and polyurethane cutting, food manufacturing, coffee essing and meat processing industries. ification reactions may require the st.

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such a high energy of activation that ed out at very high temperature and/or radicals even in the presence of a now found that if such reactions are resence of plasma in accordance with

this invention, the need for high temperature or free radical initiators may be reduced or obviated. Alternatively, the results achieved using such high temperature and/or free radical initiators may be improved. Reactions which may be carried out in this manner include, but are not limited to, hydrogenations such as of olefins, acetylenes, aldehydes, ketones, acids, anhydrides, esters, nitro compounds, nitriles, oximes, carboxylic aromatic compounds, anilines, phenols and derivatives thereof, reductive alkylation, reductive amination, dehalogenation, hydrogenolysis, isomerization, disproportionation migration, decomposition, carbonylation, decarbonylation, selective oxidation, acetoxylation and gas purification.

Whilst the present invention has particular advantages when used with reactions which have previously required high temperature and/or free radical initiation, it may also be used for reactions which do not have such a high activation energy.

Many reactions are promoted by catalysts that become deactivated with the passage of time. As described in our co-pending application, entitled "Improvements in Processes Involving Catalyst", filed on the same day as the present application, such catalyst may be regenerated by contacting the surface of the catalyst with a gas in the form of a plasma. Processes may therefore be envisaged in which both the reactant mixture for a catalysed gaseous reaction and the catalyst regeneration employ plasma.

In accordance with one aspect of such processes, the catalysed reaction may take place in one time period and the regeneration of the catalyst in a second, subsequent period. Two reactors may be employed in parallel, in one of which the reaction is taking place and in the other of which the regeneration is taking place. When the catalyst in the second reactor has been regenerated, the operations

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e aspect of such processes, the take place in one time period and e catalyst in a second, subsequent ay be employed in parallel, in one s taking place and in the other of is taking place. When the catalyst as been regenerated, the operations

in the two reactors may be reversed so that the reaction is effected over regenerated catalyst in the second reactor while the catalyst of the first reactor is regenerated. Of course, more than two reactors may be used with appropriate switching arrangements.

In some cases, the gas or gases required to regenerate the catalyst may already be included in, or readily generated from, the gaseous mixture which is to be treated in the presence of the catalyst. In such cases, a self-contained procedure can be envisaged where in one step the gaseous mixture is treated to convert to plasma the gaseous component, or at least one of the gaseous components, employed in the regeneration of the catalyst and in another step the same mixture is treated to convert to plasma at least one of the other gases of the mixture, being a gas involved in the reaction which is promoted by the catalyst. The first step may also involve a reaction to generate a required gas, e.g. the gas which is to be converted to plasma, where it is not already present as such in the reaction mixture.

An example of such a case is the detoxification of exhaust gas emissions from motor vehicles. For example, the catalyst employed in the catalytic converters fitted to motor vehicles for the detoxification of the exhaust gases tend to be deactivated with time due to poisoning by lead and/or phosphorus which are employed in additives for motor fuels.

Lead can be removed from the surface of the catalyst by the action of chlorine plasma which converts it to a soluble salt and phosphorus can be removed by the action of hydrogen plasma; the reactions proceeding according to the following equations:

$$Cl_2 \text{ ---------> } 2Cl \text{ (chlorine plasma)}$$

ıay be reversed so that the reaction is ːrated catalyst in the second reactor : the first reactor is regenerated. Of ı reactors may be used with appropriate ts.

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---> 2Cl (chlorine plasma)

Pb + 2Cl ----------> $PbCl_2$

$PbCl_2$ + 2Cl ---------> $PbCl_4$

H_2 ------------> 2H (hydrogen plasma)

P + 3H -----------> PH_3

Thus, where halogenated compounds, for example CCl_4 and H_2 are present in the exhaust gases or can be generated from a gas or gases present in these gases, it will be appreciated that the regeneration of the catalyst may be achieved using the exhaust gas itself by treating it to convert one or both of the chlorine and hydrogen components thereof to plasma.

Catalytic converter systems for motor vehicles can therefore be designed wherein the catalyst is regenerated on board the vehicle, using the vehicle engine's exhaust emissions.

Where the plasma or plasmas employed for the catalyst regeneration do not interfere with the reaction which is being promoted by the catalyst, it may even be possible to effect the catalysed reaction and the regeneration of the catalyst simultaneously.

An example of an application of the present invention to an important industrial process is in the Haber process for the catalytically promoted synthesis of ammonia from nitrogen and hydrogen. The catalyst is usually trivalent iron. Known methods require that the reaction is carried out at high temperatures and pressures such as 670K and 150 to 350 atm. Where the reaction is carried out according to the present invention, lower temperatures and pressures can be used thus reducing the risk of explosion, the energy required to carry out the synthesis and its cost.

In practice, a stoichiometric mixture of nitrogen and hydrogen is excited to plasma by any means in the presence

------> $PbCl_2$
--------> $PbCl_4$
--> 2H (hydrogen plasma)
-----> PH_3

compounds, for example CCl_4 and H_2 ust gases or can be generated from nt in these gases, it will be generation of the catalyst may be ust gas itself by treating it to he chlorine and hydrogen components

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ometric mixture of nitrogen and lasma by any means in the presence

of the catalyst to produce the ammonia. Alternatively, the admixture of hydrogen and nitrogen is excited prior to being passed over the catalyst. In this case, the catalyst will be located in a separate zone to that in which the gases are excited to plasma. The plasma is then brought into contact with the catalyst at the desired temperature and pressure. If desired, one only of the hydrogen and nitrogen is converted to plasma.

The cleavage of a carbon-carbon double bond by oxidation with ozone followed by hydrolysis to yield carbonyl compounds is an example of an application of the present invention where the moiety to be converted is a liquid. A plasma of oxygen is bubbled through a solution of the unsaturated organic compound in an inert solvent such as methanol, glacial acetic acid, ethyl acetate, hexane or chloroform at a temperature which is preferably in the region of -20°C but which may be at or above ambient temperature. The ozone is produced in the oxygen plasma.

The plasma may convert the chemical moiety to a reactive substance which then takes part in a further reaction. For example, aluminium hydride may be mixed with a catalyst poisoned with sulphur and phosphorus. The mixture is exposed to a plasma of an inert gas to decompose the aluminium hydride to aluminium and hydrogen species. These species then react with the sulphur and phosphorus poisons to form a mixture of products, namely aluminium sulphide, aluminium phosphide, hydrogen sulphide and phosphine.

Alternatively, the catalyst may be mixed with zinc oxide and exposed to a hydrogen plasma. Both reactive poisons, such as mercaptan and thiol compounds, and unreactive poisons, such as aromatic sulphur compounds can be removed from the catalyst surface by this means.

An example of the chemical moiety being converted to a

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ın and nitrogen is excited prior to
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bubbled through a solution of the
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takes part in a further reaction. For
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products, namely aluminium sulphide,
hydrogen sulphide and phosphine.

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'ogen plasma. Both reactive poisons,
nd thiol compounds, and unreactive
ətic sulphur compounds can be removed
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ıemical moiety being converted to a

reactive substance where the moiety is a liquid is where a catalyst poisoned with hydrocarbons and lead is suspended in or is in contact with dichlorine heptoxide. When the mixture is exposed to plasma of oxygen and/or inert gas, the oxygen and chlorine species formed will respectively oxidise the hydrocarbons and convert the lead to a washable lead salt.

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CLAIMS

1. A process for the conversion of a chemical moiety characterised in that the chemical moiety is in a fluid phase and said moiety is reacted with a plasma or with a reagent generated by the interaction of plasma with another component.

2. A process according to Claim 1, wherein the moiety is in liquid form and the liquid is in the form of an aerosol.

3. A process according to Claim 1, wherein the chemical moiety is a fluidised finely divided solid.

4. A process according to Claim 5, wherein the moiety is in gaseous form and is also provided in the form of plasma.

5. A process according to any one of Claims 1 to 4, wherein the plasma is generated by an AC electric field, by DC glow discharge, by a laser or by plasma torch.

6. A process according to Claim 5, wherein the plasma is generated by an AC electric field and wherein the alternating current is supplied at from 10^3Hz to 10^9Hz.

7. A process according to Claim 5, wherein the plasma is generated by an AC electric field and wherein the alternating current is supplied at from 10^9Hz to 10^{12}Hz.

8. A process according to any one of Claims 1 to 7, wherein said another component is a solid.

9. A process according to Claims 8, wherein said another component is a catalyst.

10. A process as claimed in any one of Claims 1 to 9 comprising the detoxification of a gaseous industrial

the conversion of a chemical moiety
ıt the chemical moiety is in a fluid
y is reacted with a plasma or with a
the interaction of plasma with another

ing to Claim 1, wherein the moiety is
.e liquid is in the form of an aerosol.

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1 finely divided solid.

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s also provided in the form of plasma.

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a laser or by plasma torch.

ing to Claim 5, wherein the plasma is
: electric field and wherein the
.s supplied at from 10^3Hz to 10^9Hz.

ing to Claim 5, wherein the plasma is
: electric field and wherein the
.s supplied at from 10^9Hz to 10^{12}Hz.

ding to any one of Claims 1 to 7,
component is a solid.

ing to Claims 8, wherein said another
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laimed in any one of Claims 1 to 9
xification of a gaseous industrial

emission or internal combustion engine exhaust.

11. A process according to any one of Claims 1 to 9, wherein the reaction is carried out in the presence of a catalyst.

12. A process according to Claim 11, wherein the catalyst is located in a zone remote from that in which the plasma is generated.

13. A process according to any one of Claims 1 to 12, wherein the reaction of the chemical moiety with the plasma generates a reactive species which takes part in a second reaction.

14. A process according to any one of Claims 1 to 13, wherein the conversion is carried out as a continuous, semi-continuous or batch process.

oustion engine exhaust.

ig to any one of Claims 1 to 9, carried out in the presence of a

to Claim 11, wherein the catalyst ote from that in which the plasma

to any one of Claims 1 to 12, he chemical moiety with the plasma cies which takes part in a second

to any one of Claims 1 to 13, is carried out as a continuous, process.

AMENDED CLAIMS

[received by the International Bureau on 24 January 1994 (24.01.94); original claims 1-14 amended; new claims 15-25 added (3 pages)]

1. A process for the conversion of a chemical moiety characterised in that the chemical moiety is in a fluid phase and said moiety is reacted with a plasma, or with a reagent generated by the interaction of plasma with another component, said conversion being effected in the presence of a catalyst, said catalyst being regenerated by in situ treatment with plasma.

2. A process according to Claim 1, wherein the conversion of the chemical moiety and the catalyst regeneration are carried out simultaneously.

3. A process according to Claim 1 or 2, wherein the moiety is in liquid form and the liquid is in the form of an aerosol.

4. A process according to Claim 1 or 2, wherein the chemical moiety is a fluidised finely divided solid.

5. A process according to Claim 1 or 2, wherein the moiety is in gaseous form and is also provided in the form of plasma.

6. A process according to any one of Claims 1 to 5, wherein the plasma is generated by an AC electric field, by DC glow discharge, by a laser or by plasma torch.

7. A process according to Claim 6, wherein the plasma is generated by an AC electric field and wherein the alternating current is supplied at from 10^3Hz to 10^9Hz.

8. A process according to Claim 6, wherein the plasma is generated by an AC electric field and wherein the alternating current is supplied at from 10^9Hz to 10^{12}Hz.

9. A process according to any one of Claims 1 to 8, wherein said another component is a solid.

AMENDED CLAIMS
ional Bureau on 24 January 1994 (24.01.94);
iended; new claims 15-25 added (3 pages)]

ion of a chemical moiety characterised in that the
ase and said moiety is reacted with a plasma, or with
teraction of plasma with another component, said
presence of a catalyst, said catalyst being regenerated
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m 1, wherein the conversion of the chemical moiety
: carried out simultaneously.

laim 1 or 2, wherein the moiety is in liquid form and
erosol.

n 1 or 2, wherein the chemical moiety is a fluidised

n 1 or 2, wherein the moiety is in gaseous form and
plasma.

ne of Claims 1 to 5, wherein the plasma is generated
glow discharge, by a laser or by plasma torch.

6, wherein the plasma is generated by an AC electric
; current is supplied at from 10^3Hz to 10^9Hz.

6, wherein the plasma is generated by an AC electric
; current is supplied at from 10^9Hz to 10^{12}Hz.

ne of Claims 1 to 8, wherein said another component

10. A process according to Claim 9, wherein said another component is the catalyst.

11. A process as claimed in any one of Claims 1 to 10 comprising the detoxification of a gaseous industrial emission or internal combustion engine exhaust.

12. A process according to any one of Claims 1 to 11, wherein the catalyst is located in a zone remote from that in which the plasma is generated.

13. A process according to any one of Claims 1 to 12, wherein the reaction of the chemical moiety with the plasma generates a reactive species which takes part in a second reaction.

14. A process according to any one of Claims 1 to 13, wherein the conversion is carried out as a continuous, semi-continuous or batch process.

15. A process for the detoxification of gaseous industrial emissions or internal combustion engine exhaust characterised in that the emission or exhaust is in a fluid phase and is reacted with a plasma, or with a reagent generated by the interaction of plasma with another component, in the presence of a metallic catalyst.

16. A process according to Claim 15, wherein the emission or exhaust is in liquid form and the liquid is in the form of an aerosol.

17. A process according to Claim 15, wherein the emission or exhaust is a fluidised finely divided solid.

18. A process according to Claim 15, wherein the emission or exhaust is in gaseous form and is also provided in the form of plasma.

), wherein said another component is the catalyst.

e of Claims 1 to 10 comprising the detoxification internal combustion engine exhaust.

of Claims 1 to 11, wherein the catalyst is located ı the plasma is generated.

ıne of Claims 1 to 12, wherein the reaction of the enerates a reactive species which takes part in a

one of Claims 1 to 13, wherein the conversion is ontinuous or batch process.

ıtion of gaseous industrial emissions or internal rised in that the emission or exhaust is in a fluid or with a reagent generated by the interaction of the presence of a metallic catalyst.

ı 15, wherein the emission or exhaust is in liquid f an aerosol.

5, wherein the emission or exhaust is a fluidised

5, wherein the emission or exhaust is in gaseous m of plasma.

19. A process according to any one of Claims 15 to 19, wherein the plasma is generated by an AC electric field, by DC glow discharge, by a laser or by plasma torch.

20. A process according to Claim 19, wherein the plasma is generated by an AC electric field and wherein the alternating current is supplied at from 10^3Hz to 10^9Hz.

21. A process according to Claim 19, wherein the plasma is generated by an AC electric field and wherein the alternating current is supplied at from 10^9Hz to 10^{12}Hz.

22. A process according to any one of Claims 15 to 21, wherein said another component is a solid.

23. A process according to Claim 22, wherein said another component is the catalyst.

24. A process according to any one of Claims 15 to 23, wherein the reaction of the emission or exhaust with the plasma generates a reactive species which takes part in a second reaction.

25. A process according to any one of Claims 15 to 24, wherein the conversion is carried out as a continuous, semi-continuous or batch process.

any one of Claims 15 to 19, wherein the plasma is field, by DC glow discharge, by a laser or by plasma

Claim 19, wherein the plasma is generated by an AC alternating current is supplied at from 10^3Hz to 10^9Hz.

Claim 19, wherein the plasma is generated by an AC alternating current is supplied at from 10^9Hz to 10^{12}Hz.

any one of Claims 15 to 21, wherein said another

laim 22, wherein said another component is the catalyst.

any one of Claims 15 to 23, wherein the reaction of the plasma generates a reactive species which takes part in

o any one of Claims 15 to 24, wherein the conversion is semi-continuous or batch process.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 93/01641

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^5: B 01 D 53/00, B 01 D 53/32, B 01 D 53/34, B 01 D 53/36, B 01 J 19/08, H 05 H 1/24, C 10 G 15/12

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^5	B 01 D, B 01 J, H 05 H, C 10 G, B 29 C, C 08 J, C 23 C, A 61 L

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	US, A, 5 026 949 (AMOUROUX) 25 June 1991 (25.06.91), claims. --	1,2,8, 9,11-14
X	US, A, 5 015 349 (SUIB) 14 May 1991 (14.05.91), claims. --	1,4,7, 11,12
X	US, A, 4 941 965 (AMOUROUX) 17 July 1990 (17.07.90), claims. --	1,2,8, 9,11
X	EP, A1, 0 366 876 (MITSUBISHI JUKOGYO KABUSHIKI KAISHA) 09 May 1990 (09.05.90), claims. --	1,4,5, 10
X	US, A, 3 419 597	1,4,11

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
11 October 1993	22. 11. 93
International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	BECKER e.h.

AL SEARCH REPORT

International Application No PCT/GB 93/01641

classification symbols apply, indicate all) [6]

National Classification and IPC

32,B 01 D 53/34,B 01 D 53/36,
4,C 10 G 15/12

umentation Searched [7]

Classification Symbols

H,C 10 G,B 29 C,C 08 J,C 23 C,

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nents are Included in the Fields Searched [8]

appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
ne 1991	1,2,8, 9,11-14
91	1,4,7, 11,12
ly 1990	1,2,8, 9,11
GYO KABUSHIKI 990	1,4,5, 10
	1,4,11

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of Mailing of this International Search Report

22. 11. 93

Signature of Authorized Officer

BECKER e.h.

International Application No PCT/GB 93/01641

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages	Relevant to Claim No.
	(BEGLEY) 31 December 1968 (31.12.68), claims. --	-13
X	DE, A1, 3 206 785 (VILLAMOSIPARI KUTATO INTEZET) 28 October 1982 (28:10.82), the whole document. --	1,2
X	US, A, 4 469 508 (AMOUROUX) 04 September 1984 (04.09.84), claims. ----	1,3

International Application No PCT/GB 93/01641

RELEVANT (CONTINUED FROM THE SECOND SHEET)	
indication, where appropriate, of the relevant passages	Relevant to Claim No.
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508) 04 September 1984), ----	1,3

ry 1985)

ANHANG	ANNEX	ANNEXE
zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.	to the International Search Report to the International Patent Application No.	au rapport de recherche international relatif à la demande de brevet international n°

PCT/GB 93/01641 SAE 77571

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The Office is in no way liable for these particulars which are given merely for the purpose of information.

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les reseignements fournis sont donnés à titre indicatif et n'engagent pas la responsibilité de l'Office.

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